Interconversion of Five- and Seven-membered Cyclic Azo-compounds: A 1,3-Azo-group Migration studied by High-speed Liquid Chromotography

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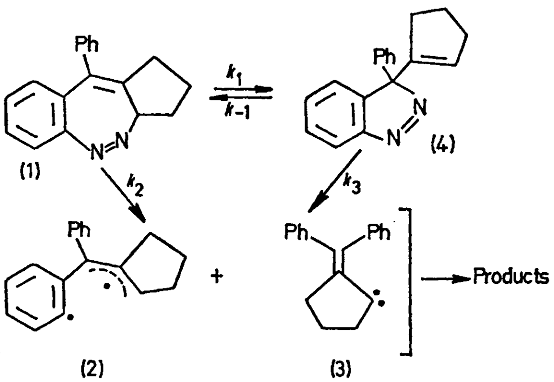
Summary The decomposition of the 3*H*-1,2-benzodiazepine (**1**) is accompanied by its faster equilibration with the isomeric 3*H*-indazole (**4**) *via* a 1,3-shift of the azo group; the establishment of equilibrium and the decomposition have been monitored by high-speed liquid chromatography (h.s.l.c.).

We have recently shown that the thermolysis of 3*H*-1,2-benzodiazepines, *e.g.* (**1**), gives mixtures of hydrocarbon products formed *via* the intermediates (**2**) and/or (**3**).[1] Further investigation into the mechanism of this reaction using high-speed liquid chromatography (h.s.l.c.) has revealed that the loss of nitrogen from (**1**) is accompanied by the rapid equilibration of (**1**) with the isomeric 3*H*-indazole (**4**).

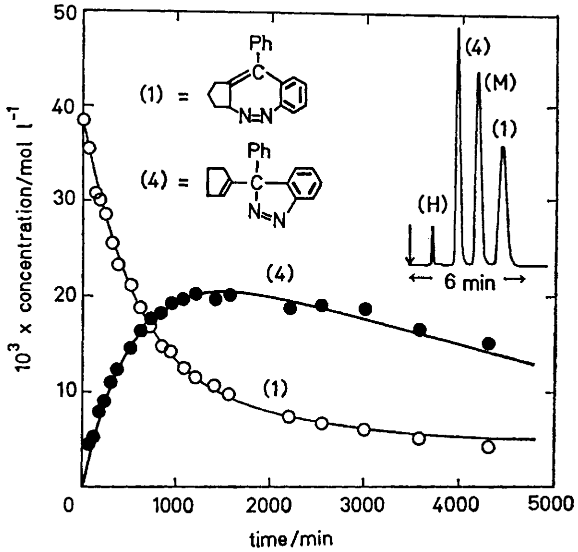


Scheme

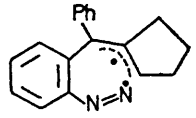
The indazole (m.p. 66—67°) is an unstable colourless compound which has been isolated by chromatography from a mixture of (**1**) and (**4**) produced by the gas-phase pyrolysis of (**1**) at *ca.* 250°. Its structure follows from its n.m.r. and mass spectra. In the ^1H n.m.r. spectrum the olefinic proton (τ 4·45) has a similar chemical shift to that of the analogous proton in 1-methylcyclopentene (τ 4·68), and in the ^{13}C resonance spectrum the absorption due to the C-3 tertiary carbon (99·8 p.p.m. from Me_4Si) is close to that of the C-3 carbon in 3,3-diphenyl-4,7-dimethoxy-3*H*-indazole (103·3 p.p.m. from Me_4Si). The mass spectrum shows a small parent ion (*ca.* 1%, *m/e* 260), a large peak (76%) at *m/e* 232 due to loss of N_2 from the parent ion, and the base peak at *m/e* 204.

We have used h.s.l.c. to monitor the thermolysis of (**1**) in hexadecane at 133° with the result shown in the Figure. The diazepine isomerises to (**4**) about four times as fast as nitrogen is lost. A similar experiment starting with the indazole (**4**) clearly confirmed the reverse isomerisation and the tendency toward an equilibration of (**1**) and (**4**).

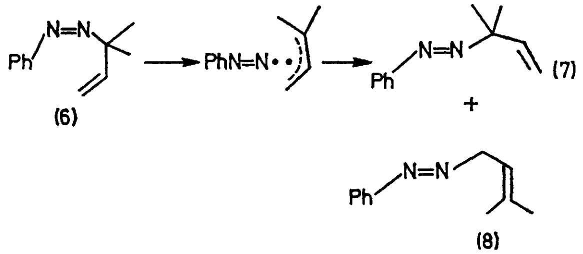
The general reaction scheme may therefore be represented by reactions (1), (—1), (2), and (3). Analysis of the experimental data (the points in the Figure) in terms of the Scheme using the CHEKMAT computer program[2] with complete freedom in the choice of rate constants, gave the following values for the best fit: $k_1 = 12{\cdot}1 \times 10^{-4}$, $k_{-1} = 4{\cdot}4 \times 10^{-4}$, $k_2 = 1{\cdot}6 \times 10^{-4}$, $k_3 = 1{\cdot}5 \times 10^{-4}\ \mathrm{min}^{-1}$. These values produce the full lines shown in the Figure. We emphasise, however, that the values of k_2 and k_3 are strongly correlated and that the relative values quoted above have little chemical significance. Thus the data can be fitted almost as well if k_3 is arbitrarily taken as zero: the values for best fit then become $k_1 = 12{\cdot}0 \times 10^{-4}$, $k_{-1} = 5{\cdot}6 \times 10^{-4}$ $k_2 = 3{\cdot}3 \times 10^{-4}\ \mathrm{min}^{-1}$. Evidently we cannot establish from the present data whether the final hydrocarbon products come from decomposition of (**1**) or (**4**) or of both species. What is certain, however, is that equilibration of



Figure



(5)



(**1**) with (**4**) proceeds about four times as fast as the decomposition and that the equilibrium constant K_1 $(=k_1/k_{-1})$ lies between 2 and 3. Further work on the reaction starting with the indazole (**4**) is required to give proper discrimination of k_2 from k_3.

The h.s.l.c. analysis was carried out on a 660 × 2 mm glass column packed with Corasil II using hexane–methylene chloride (60 : 40) as mobile phase. The insert to the Figure shows a typical separation of hydrocarbon product (H) from (**1**) and (**4**), and from diethyl phthalate (M) used as internal standard. Peak areas were used for quantitation after calibration with pure compounds.

H.s.l.c. has proved of immense value for this type of study involving labile reactants and we believe that this is the first time it has been used in a kinetic study to derive accurate rate constant data.

The interconversion of (**1**) and (**4**) is an unprecedented equilibration between five- and seven-membered cyclic azo-compounds and formally involves a 1,3-azo-group migration. The isomerisation of (**1**) is induced by light as well as by heat and although it is premature to discuss the mechanism at this time it seems more likely that the reaction takes place *via* the diradical (**5**) than by a concerted process. Attempts to detect (**5**) by e.s.r. spectroscopy are presently in progress. Diradicals and radical-pair intermediates have recently been suggested for the irreversible ring expansion of 3-vinyldiazirine to pyrazole[3] and for the conversion of (**6**) into (**7**) and (**8**) at 0°.[4]

(*Received*, 1*st April* **1974**; *Com.* **363**.)

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